



(11) (A) No.

1 265 464

(45) ISSUED 700206

(52) CLASS 196-97

4

(51) INT. CL. C10G 11/05

(19) (CA) **CANADIAN PATENT** (12)

(54) Residual Oil Cracking Process Using Dry Gas as Lift
Gas Initially in Riser Reactor

(72) Kmecak, Ronald A.;
Hettinger, William P., Jr.;
Kovach, Stephen M.;
Fraley, Larry M.,
U. S. A.

(73) Granted to Ashland Oil, Inc.
U. S. A.

(21) APPLICATION No. 466,631

(22) FILED 841030

(30) PRIORITY DATE (US) U. S. A. (06/620, 196) 840613

No. OF CLAIMS 31

Canada

ABSTRACT

Wet gas (containing little C3+ and almost no C5+) is substituted for wet gas (generally containing C3+ and C5+) and used as the lift gas for transporting catalyst through a hydrocarbon conversion riser e.g. metal removal system, fluid catalytic cracker, and RCCSM heavy oil cracking process. Preferably the hydrocarbon feed contacts the catalyst-lift gas mixture after some period of acceleration and mixing and passivation of contaminants on the catalyst surface. Advantages include lower gasing and lower coke-make as well as better product selectivity.

Preferred catalyst-lift gas contact times are from about 0.01 to 2, more preferably 0.05 to 1.5, and most preferably 0.15 to 1 second. Preferred lift gas hydrogen contents are at least about 10, more preferably 15 and most preferably 20 mol percent hydrogen.

6224aus/application

RI-6224A

1265464

Residual Oil Cracking Process Using Dry Gas
As Lift Gas Initially In Riser Reactor

BACKGROUND OF THE INVENTION

(I) Field Of The Invention:

5 The invention relates to a novel and improved
method for effecting the catalytic cracking of fractions
of crude oil and particularly residual portions of crude
oils comprising gas oils which may or may not comprise
vacuum resid including asphaltenes, asphalt, substantial
10 metal contaminants of nickel and vanadium, sulfur and
nitrogen compounds. The hydrocarbon feed may be a 343°C
(650°F) plus carbometallic containing heavy oil feed
providing very little or substantial amounts of
Ramsbottom carbon or Conradson carbon contributing
15 materials. The crude oil fraction employed in the
cracking operation of this invention may be a reduced
crude, a topped crude, vacuum residues, heavy oil
extracts of tar sands, a coal liquefaction product, oil
product of oil shale pyrolysis and mixtures thereof. A
20 typical oil feed may boil from 343°C (650°F) up to 566°C
(1050°F) or as high as 816°C (1500°F) when including
vacuum bottoms.

 In a more particular aspect, the invention
relates to improving the product selectivity obtained and
25 maintaining desired equilibrium catalyst activity during
the cracking of such heavy oil feeds with particularly an
active crystalline zeolite containing catalyst. The
essence of the invention is achieved by initially forming
an upflowing suspension of regenerated catalyst particles

of desired high elevated temperature in a lift gas comprising a dry gas composition contributing little, if any, coke to the catalyst suspension before effecting contact with the oil feed charged to a riser catalytic cracking operations.

The present invention is concerned with and relates to the field of hydrocarbon conversion disclosed in U.S. Patent 4432863; U.S. Patent 4419223; and U.S. Patent 4435279. The invention also particularly relates to the combination operation of residual oil feed treatment to partially decarbonize and demetallize before effecting catalytic cracking, thereof, disclosed in U.S. Patent 4525268; and U.S. Patent 4569753. It also relates to the field of invention disclosed in U.S. Patent 4341624; U.S. Patent 4347122; U.S. Patent 4299687; U.S. Patent 4354923; U.S. Patent 4332673; U.S. Patent 4419223; U.S. Patent 4435279 and U.S. Patent 4434044.

B

(II) Description Of Prior Art

The prior art briefly discussed below, is also acknowledged as having been considered during identification of the invention herein disclosed.

5 US 2,900,326 to Gilmore (Phillips) processes a gas oil in an FCC unit and the hydrogen containing light gases produced are recycled admixed with the fresh feed charged to suppress C1-C4 formation.

10 US 2,904,504 to Rice (Gulf) admixes C1-C5 hydrocarbons with hot regenerated catalyst recycled to a riser cracking step and prior to the oil feed injection point to the riser. The light hydrocarbons are fed at a rate of about 35.6 to 89.0 cubic meters per cubic meter of feed (about 200 to 500 cubic feet per barrel of feed).
15 (All references to "barrel" herein refer to barrels of feed unless otherwise expressly noted.

 US 3,849,932 to Owen (Mobil) introduces light hydrocarbons to the bottom of a riser cracking zone. He also introduces a gas oil further up the riser, followed
20 by hydrocarbon injection still further up the riser. The suspended catalyst moves upwardly by these injection points and is lifted by vaporous hydrocarbons and charged light hydrocarbons.

 US 2,888,395 to Henny (UOP) contacts a heavy
25 hydrocarbon with a catalyst in the presence of substantially pure hydrogen in a riser. The hydrogen is produced outside the cracking unit. The use of hydrogen

with the oil feed is said to reduce coke make and to reduce the production of unsaturated products.

5 US 4,268,416 to Stine (UOP) reduces catalyst contaminated with nickel and vanadium by contacting the catalyst with water-saturated hydrogen prior to introduction of the catalyst into the riser cracking zone.

10 US 4,280,895 and US 4,280,896, both to Stuntz (Exxon) pass metal contaminated cracking catalyst from the riser cracking zone to a regeneration zone where coke is burned off. The regenerate catalyst is then treated with hydrogen, carbon monoxide or hydrogen-carbon monoxide mixture in a reduction zone prior to its introduction into the riser cracking zone.

15 US 4,345,992 (Phillips) transfers regenerated catalyst to a reduction zone where the catalyst is contracted with hydrogen. The reduced catalyst and unconsumed hydrogen are then transferred to the riser cracking zone.

20 US 4,361,496 to Castillo (UOP) treats regenerated-metal contaminated catalyst with a hydrocarbon gas comprising three carbon atoms or less, or a mixture thereof, to achieve complete reduction of contaminant metals which are carbonized in the dipleg
25 located between the regenerator and the riser reaction zone. This dipleg is used to convey catalyst from the regenerator to the riser cracking zone.

US 4,364,848 to Castillo (UOP) is similar to
US 4,361,496 above in that the reducing gas used is a
mixture of one, two, three carbon atoms to passivate the
metals to the metallic state before carbonization
5 thereof.

US 2,937,988 (Esso Res. & Eng. Co.)
discloses a riser reactor system for cracking an oil feed
such as a heavy hydrocarbon residuum, vacuum or
atmospheric crude bottom, pitch, asphalt or mixtures
10 thereof wherein hot coke particles are initially
dispersed in fluidizing gases such as steam, light
hydrocarbons, an inert gas or mixtures thereof.

US 3,406,112 (Mobil) discloses recovering a
hydrocarbon product stream boiling below about C6 or C5
15 hydrocarbons which are employed in an amount sufficient
to form a suspension with zeolite catalyst particles in a
lower portion of a riser reaction zone before charging
the oil feed in contact therewith.

US 3,849,291 (Mobil) discloses the use of dry
20 gas or wet gas products of cracking as diluent material
in the riser cracking operation disclosed.

US 3,894,932 (Mobil) discloses the use of a
C3-C4 hydrocarbon gas mixture in the bottom portion of
a riser to form an upflowing suspension of zeolite catalyst
25 particles prior to contact with an oil feed.

US 2,684,931 (Union Oil) is directed to a
fluidized solids process where a gaseous product of

cracking compromising hydrogen, methane, unsaturated and saturated normally gaseous hydrocarbons are used.

US 4,431,515 (Ashland Oil, Inc.) is directed to a carbometallic oil conversion process using hydrogen in a riser reactor and comprising a high metals containing catalyst. This patent discloses the addition of hydrogen to the riser reaction zone to reduce the formation of conjugated diolefins. Thus, it is postulated that the concentration of diolefins is reduced and coke production with the metals containing catalyst is also reduced. The patent discusses the use of hydrogen gas admixed with the hydrocarbon feed provided by gas streams comprising 60 and 80% or more hydrogen. The patent is silent with respect to the essence of invention described in the present application.

None of the prior art briefly discussed above suggest or teach the striking and unexpected improved results obtained by applicants concept of invention employing a particular dry gas composition in combination with a cooling fluid to form an upflowing desired high temperature regenerated catalyst suspension suitable for more particularly optimizing the product selectivity obtainable of a given hydrocarbon feed catalytic conversion operation.

In general, gasoline and other liquid hydrocarbon fuels boil in the range of about 38°C (100°F) to about 343°C (about 650°F), however, the crude oil from which these fuels are made is a diverse mixture of hydrocarbons and other compounds which vary widely in molecular weight and therefore boil over a wider range.

RI-6224A

B

For example, crude oils are known in which 30% to 60% or more of the total volume is composed of compounds boiling at temperatures above 343°C (650°F). Among these crudes are crudes in which about 10% to about 30% or more of the total volume consists of compounds which are so heavy in molecular weight that they boil above 552°C (1025°F), or at least will not boil below 552°C (1025°F) at atmospheric pressure.

Because these relatively abundant high boiling components of crude oil are unsuitable for inclusion in gasoline and other liquid hydrocarbon fuels, the Fluid Catalytic Cracking (FCC) process was developed for cracking or breaking the molecules of high molecular weight, high boiling compounds into smaller molecules which boil over an appropriate boiling range. Although the FCC process has reached a highly advanced state, and many modified forms and variations have been developed, their unifying factor is that a vaporized hydrocarbon feedstock which contains high molecular weight, high boiling components is caused to crack at an elevated temperature in contact with a cracking catalyst that is suspended in the feedstock vapors. Upon attainment of the desired molecular weight and boiling point reduction, the catalyst is separated from the desired products.

The present invention is concerned with using hydrocarbon feedstocks which have Ramsbottom carbon values which exhibit a substantially greater potential for coke formation than does the usual FCC feedstock. In conventional FCC practice, Ramsbottom carbon values on the order of about 0.1 to about 1.0 are regarded as indicative of acceptable feed. Conventional FCC practice

has employed as feedstock that fraction of crude oil which boil at about 343°C (650°F) to about 538°C (1000°F), and is relatively free of coke precursors and heavy metal contaminants. Such feedstock, known as "vacuum gas oil" (VGO), is generally prepared from crude oil by distilling off the fractions boiling below about 343°C (650°F) at atmospheric pressure and then separating, by further vacuum distillation from the heavier fractions, a cut boiling between about 343°C (650°F) and about 482°C (900°F) to 552°C (1025°F).

Since the various heavy metals in carbometallic oil are not of equal catalyst poisoning activity, it is convenient to express the poisoning activity of an oil containing a given poisoning metal or metals in terms of the amount of a single metal which is estimated to have equivalent poisoning activity. Thus, the heavy metals content of an oil can be expressed by the following formula (patterned after that of W. L. Nelson in Oil and Gas Journal, page 143, Oct. 23, 1961) in which the content of each metal present is expressed in parts per million of such metal, as metal, on a weight basis, based on the weight of feed.

$$\text{Nickel Equivalents} = \text{Ni} + (\text{V}/4.8) + (\text{Fe}/7.1) + (\text{Cu}/1.23)$$

The above formula can also be employed as a measure of the accumulation of heavy metals on the cracking catalyst, except that the quantity of metal employed in the formula is based on the weight of catalyst (moisture free basis) instead of the weight of feed.

The present invention is concerned with the processing of feedstocks containing heavy metals substantially in excess of that in conventional FCC processing, and which therefore have potential for accumulating on and poisoning the catalyst.

SUMMARY OF THE INVENTION

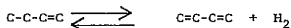
The present invention is notable in providing a simple, relatively straightforward and highly productive approach to the conversion of oil feeds to various lighter products, such as gasoline. The feedstock is comprised of oil which boils above about 343°C (650°F). Such oil, or at least the 343°C+ (650°F) portion thereof, is characterized by a heavy metals content of at least about 4, preferably more than about 5, and most preferably at least about 5.5 ppm Nickel Equivalents of heavy metals by weight and by a carbon residue on pyrolysis of at least about 1% and more preferably at least about 2% by weight or more.

A catalyst which contains from about 1000 to about 70,000 ppm of metals such as nickel, incremented iron, copper and/or vanadium or its oxides is referred to herein as a contaminated catalyst because such catalyst tends to encourage unless passivated the formation of coke during the cracking process. Thus, in most instances, the catalyst is continuously replaced to maintain these metals in low concentrations on the catalyst up to 20,000 ppm Ni + V.

In the present invention, it is preferred to use a catalyst which contains these metals, especially in

the above concentration range, because they are considered to have the ability to activate hydrogen, when hydrogen is introduced in the cracking system.

- One mechanism which has been proposed as representing a means by which coke is formed during the catalytic cracking process is that conjugated diolefins, such as butadiene, form during the cracking process, either through dehydrogenation, or further cracking of the olefins present in the feed via carbonium ion mechanisms. The diolefins are believed to condense to form carbonaceous material, which accumulate on the catalyst, inactivating it. The overall chemical reaction can be written as follows:



- In the presence of a metal contaminated catalyst, the above reaction is expected to accelerate as do coking and other dehydrogenation reactions. However, based on LeChatalier's principle, the presence of hydrogen in the system tends to reverse the reaction and reduce the formation of conjugated diolefins. A retardation in the formation of conjugated diolefins inhibits fouling reactions while facilitating or enhancing other carbonium ion mechanisms thereby producing more valuable products.

- A second reaction, also based on LeChatalier's principle, is also inhibited by the addition of hydrogen to the catalytic cracking system. Many of the metals referred to above return to the reactor as oxides and are undoubtedly reduced quickly to metals or lower valent

oxides in the reactor by scavenging of the hydrogen produced in the above reaction. The driving force for such reaction, therefore, is also to the right in the above equation and this driving force may also encourage the formation of conjugated diolefins.

Thus, while not wishing to be bound by theory, it is postulated that when hydrogen gas is added to a catalytic cracking system which contains a catalyst contaminated with metals such as nickel, copper, iron and vanadium or its oxides, the conjugated diolefin reaction is reversed, the concentration of diolefins is reduced and coke production is also reduced. In addition, olefins that would normally be converted to diolefins and be removed from the system may remain as olefins, which are then free to interact with Bronsted acids, thereby enhancing conversion and selectivity. A mixture of feed, catalyst, and gas is introduced into a progressive flow type reactor.

At the end of a predetermined riser residence time, the catalyst is projected in a direction established by the elongated riser reaction zone or an extension, thereof, whereby vaporous products, having lesser momentum, are caused to make a change of direction, resulting in ballistic separation of products from catalyst, thus avoiding secondary cracking of products.

The separated catalyst is stripped to remove high boiling components and other entrained or absorbed hydrocarbons, and then regenerated by burning the coke in at least one regeneration zone with an oxygen-containing

combustion-supporting gas under conditions of time, temperature and atmosphere sufficient to reduce the carbon on the regenerated catalyst to about 0.05% or less by weight. The coke is burned in a zone wherein the molar ratio of $\text{CO}:\text{CO}_2$ is maintained at a level of at least about 0.20 to about 0.25, more preferably at least about 0.3 and still more preferably at least about 0.5.

The regenerated catalyst is stripped to remove entrained air, and thereafter recycled to the reactor for contact with fresh feed.

The present invention is directed to maintaining a special relationship in operating parameters in the hydrocarbon feed catalytic cracking step which thereby affects the severity of the catalyst regeneration required and employed. Thus, a substantial improvement in hydrocarbon product selectivity is achieved at reduced coke make by the catalyst activity charged to the oil feed cracking operation. The method of operation of this invention provides a catalyst which is of a higher order of activity than previously achieved.

In a particular aspect the present invention is concerned with effecting more selective crystalline zeolite catalytic cracking of residual oil fractions of crude oils particularly comprising nickel and vanadium metal contaminants in an amount within the range of 1000 to 20,000 ppm in combination with high molecular weight polycyclic hydrocarbon materials contributing a Ramsbottom carbon value up to about 8 during catalytic cracking thereof.

In a more particular aspect the present invention is concerned with using a dry gas stream comprising hydrogen with some limited C_3 -plus carbon producing components therein under catalyst suspension forming conditions. A combination of one or more regenerated catalyst cooling fluids such as steam, water and combinations thereof is used with the dry gas to form a rising suspension with hot regenerated catalyst particles adjusted to a temperature particularly suitable for effecting catalytic cracking of a residual oil feed comprising gas oils with or without higher boiling vacuum bottoms generally boiling above about $552^{\circ}C$ ($1025^{\circ}F$). A gas stream suitable for the purpose and essence of this invention is a commercially available refinery product dry gas stream comprising less than 10 vol. % of C_3 plus hydrocarbons and preferably comprises hydrogen in an amount of at least 10 vol. %. Such a hydrogen containing gas is economically recoverable from one or more refinery gas streams.

The advantages obtained by the combination operation of the present invention using a dry gas stream with steam and/or water in place of naphtha, light hydrocarbon, a high purity hydrogen gas or a wet gas stream comprising substantial C_3 plus hydrocarbon component are unexpected and not predictable. In fact, there is some considerable published prior art which suggests that a metal contaminated cracking catalyst should comprise some considerable residual coke, thereon, to suppress the hydrogenating and dehydrogenating functions of the metal contaminants. However, applicants operating technique has produced unexpected liquid

product selectivity results with a relative inexpensive dry gas product at substantially reduced coke make.

CATALYST CHARACTERISTICS

5 The catalyst employed in the catalytic cracking-hydrocarbon conversion operation of the present invention may be substantially any fluid crystalline zeolite cracking catalyst of the prior art comprising rare earth and/or hydrogen ions in the crystal structure of the zeolite. The zeolite is dispersed in a
10 siliceous-clay matrix material which may or may not provide some cracking activity. That is, the matrix may be selected from silica-alumina, silica-zirconium or silica-chromium mixture which is promoted with one or more metal additives which are effective in passivating
15 accumulated metal contaminants. Some additive material which may be used include rare earth metals providing excess lanthanum, and compounds of antimony and titanium. The cracking catalyst employed in the method of this invention may comprise the active crystalline zeolite
20 component in an amount less than about 40 wt. % and more usually in an amount within the range of 5 to 20 wt. % as equilibrium catalyst.

In a more particular aspect, the catalyst employed may be selected from one described in U.S.
25 4,440,868 or U.S. 4,435,515. A preferred catalyst may be one selected from U.S. 4,480,047.

RI-6224A

B

A particularly preferred class of catalysts includes those that are capable of activating hydrogen and that have pore structures into which molecules of feed may enter for adsorption and/or for contact with active catalytic sites within or adjacent the pores. Various types of catalysts are available within this classification, including for example the layered silicates, e.g. smectites.

The zeolite-containing catalysts used in the present invention may include any zeolite, whether natural, semi-synthetic or synthetic, alone or in admixture with other materials which do not significantly impair the suitability of the catalyst, provided the resultant catalyst has the activity and pore structure referred to below. For example, if the catalyst is a mixture, it may include the zeolite component associated with or dispersed in a porous refractory inorganic oxide carrier; in such case the catalyst may for example contain about 1% to about 60%, more preferably about 1 to about 40% and most typically about 5 to about 40% by weight of the zeolite dispersed in the carriers, based on the total weight of catalyst (water free basis) of the porous refractory inorganic oxide alone or in combination with any of the known adjuvants for promoting or suppressing various desired and undesired reactions, some of which are discussed below.

For a general explanation of the genus of zeolite molecular sieve catalysts useful in the invention, attention is drawn to the disclosures of the articles entitled "Refinery Catalysts Are a Fluid Business" and "Making Cat Crackers Work on Varied Diet",

appearing respectively in the July 26, 1978 and Sept. 13, 1978 issues of Chemical Week magazine.

5 In general, it is preferred to employ catalysts having an overall particle size in the range of about 5×10^{-6} meters to about 160×10^{-6} meters (about 5 to about 160 microns), more preferably about 40×10^{-6} meters to about 120×10^{-6} meters (about 40 to about 120 microns),
10 and containing a proportionately major amount in the 40×10^{-6} meters to about 80×10^{-6} meters (40 to about 80 microns) range.

It is preferred to employ a catalyst initially having a relatively high level of cracking activity and selectivity, and providing high levels of conversion and productivity at low residence times. The conversion capabilities of the catalyst may be expressed in terms of the conversion produced during actual operation or by standard catalyst activity test. (See the classical
20 Shankland and Schmitkors "Determination of Activity and Selectivity of Cracking Catalyst", Proc. API 27 (III), 1947, pp. 57-77). For example, it is preferred to employ catalysts which, in the course of extended operation in the process, are sufficiently active for sustaining a
25 level of conversion of at least about 50% or more preferably at least about 60%. In this connection, conversion is expressed in liquid volume percent, based on fresh feed.

The preferred catalyst may also be defined as
30 one which, in its virgin or equilibrium state, exhibits a

RI-6224A

B

specified activity expressed as a volume percentage derived by the MAT (micro-activity test). For a discussion relating to performing MAT's, and their significance to the present invention (see U.S. 4,299,687).

When characterized on the basis of MAT activity, the preferred catalysts may be described on the basis of their MAT activity "as introduced" into the process of the present invention, or on the basis of their "as withdrawn" or equilibrium MAT activity, or on both of these bases.

A preferred MAT activity for virgin and non-virgin catalyst "as introduced" in the process of the present invention is at least about 60%, but it will be appreciated that, particularly in the case of non-virgin catalysts supplied at high addition rates, lower MAT activity levels may be acceptable.

An acceptable equilibrium MAT activity level of catalyst which has been used in the process of the present invention is above 20%, preferably at least about 40% or more preferably about 60% or more are preferred values.

CATALYST ADDITION

In general, the weight ratio of catalyst to fresh feed (feed which has not previously been exposed to cracking catalyst under cracking conditions) used in the present invention is in the range of about 3 to 18. Preferred ratios may be about 4 to 12, depending on the

- coke forming tendencies of the feed. Within the limitations of product quality requirements, controlling the catalyst to oil ratio at relatively low levels within the aforesaid ranges tends to reduce the coke yield of the oil, based on fresh feed.

- Catalyst may be added continuously or periodically, such as, for example, to make up for normal losses of catalyst from the system. Moreover, catalyst addition may be conducted in conjunction with withdrawal of catalyst, such as, for example, to maintain or increase the average activity level of the catalyst in the unit or to maintain a constant amount of metal on catalyst.

- For example, the rate at which virgin catalyst is added to the unit may be in the range of about .285 kilograms per m^3 of feed (0.1 to about 3 lb/bbl) to about 8.55 kilograms per cubic meter of feed or more (about 0.03 to 1 weight % of the feedstock) or more, depending on metal content in the feed, and the level of metal allowed to reside on the equilibrium catalyst. If, on the other hand, equilibrium catalyst is employed, a replacement rate as high as about 14.25 kilograms per cubic meter of feed (about 5 pounds per barrel) or more can be practiced. Where circumstances are such that the conditions in the unit tend to promote more rapid deactivation, one may employ rates of addition greater than those stated above; but in the opposite circumstances, lower rates of addition may be employed.

METAL-ON-CATALYST

The invention may be practiced with catalyst bearing accumulations of heavy metals which heretofore would have been considered quite intolerable in conventional fluid catalytic cracking (FCC), vacuum gas oil (VGO) operations. Employing catalyst bearing heavy metals accumulations in the range of about 1000 to about 20,000 ppm Ni+V on the average, is contemplated. The accumulation may also be in the range of about 4000 to 50,000 ppm and more likely in the range of 5000 to about 30,000 ppm. The higher foregoing ranges are based on parts per million of heavy metal, including nickel, vanadium, incremental iron (that additional iron accumulated while being used) and copper, in which the metals are expressed as metal, by weight, measured on and abased on regenerated equilibrium catalyst, i.e. previously used catalyst. One might employ equilibrium catalyst from another unit, for example, an FCC unit which has been used in the cracking of a vacuum gas oil, having a carbon residue on pyrolysis of less than 1 and containing less than about 4 ppm Nickel Equivalents of heavy metals.

CATALYST PROMOTERS

The catalyst composition may also include one or more combustion promoters which are useful in the subsequent step of regenerating the catalyst. In order to restore the activity of the catalyst, coke is burned off in a regeneration step, in which coke is converted to combustion gases including carbon monoxide and/or carbon dioxide. Various substances e.g. Pt, Pd, rare earths,

are known which, when incorporated into a cracking catalyst in small quantities (or added with the feed stock), tend to promote conversion of coke to carbon monoxide and/or carbon dioxide. Promoters of combustion
5 to carbon monoxide tend to lower the temperature at which a given degree of coke removal can be attained, thus diminishing the potential for thermal deactivation of the catalyst.

Such promoters, normally used in effective
10 amounts ranging from a trace up to about 10% to 20% by weight of catalyst, may, for example, be of any type which generally promotes combustion of carbon under regenerating conditions.

ADDITIONAL MATERIALS

15 The amount of additional materials which may be present in the feed may be varied as desired; but said amount will preferably be sufficient to substantially heat balance the process. These materials may for example be introduced into the reaction zone in a weight
20 ratio relative to feed of up to about 0.4, preferably in the range of about 0.02 to about 0.4, more preferably about 0.03 to about 0.3 and most preferably about 0.05 to about 0.25.

When liquid water, recycled from the
25 regeneration step, is added to the reaction zone as an additional material, either already admixed with the feed or separately, a preferred embodiment is to have hydrogen sulfide dissolved therein within the above ranges, based on the total amount of feed. Alternately, about 500 ppm

to about 5000 ppm of hydrogen sulfide should be dissolved
- in the recycled liquid water. Hydrogen sulfide gas, in
the above weight ratio ranges, may also be added as the
additional material instead of hydrogen sulfide dissolved
5 in recycled liquid water.

The process of the present invention employees
ballistic separation of catalyst and vapors at the
downstream end of a progressive flow type riser, such as
is taught in U.S. 4,066,533 and 4,070,159 to Myers et al.
10

However, depending upon whether there is
slippage between the catalyst and hydrocarbon vapor in
the riser, the catalyst riser residence time may or may
15 not be the same as that of the vapor. Thus, the ratio of
average catalyst reactor residence time versus vapor
reactor residence time, i.e. slippage, may be in the
range of about 1 to about 5, more preferably about 1 to
about 4, and most preferably about 1.1 to about 3, with
20 about 1.2 to about 2 being the preferred range.

It is considered advantageous if the vapor riser
residence time and vapor-catalyst contact time in the
riser are substantially the same for at least about 80%
of the riser length.

25

CATALYST REGENERATION

Regeneration of catalyst may be performed at a
temperature in the range of about 593°C (1100°F) to about
871°C (1600°F), measured at the catalyst regenerator

RI-6224A

B

outlet. This temperature may be in the range of about 649°C (1200°F) to about 816°C (1500°F), more preferably in the range of about 677°C (1250°F) to about 774°C (1425°F) and optimally about 704°C (1300°F) to about 5 746°C (1375°F) or about 760°C (1400°F).

To minimize regeneration temperatures and demand for regeneration capacity, it is desirable to employ conditions of time, temperature and atmosphere in a stripper which are sufficient to reduce potentially 10 volatile hydrocarbon material borne by the stripped catalyst to about 10% or less by weight carried to the regenerator. Such stripping may for example include reheating of the catalyst, extensive stripping with steam, the use of gases having a temperature considered 15 higher than normal for FCC/VGO operations, such as for instance flue gas from the regenerator, as well as other refinery stream gases such as hydrotreater off-gas (H₂S containing), hydrogen and others. The stripper may be operated at a temperature above about 482°C (900°F). 20 Stripping operations in which the temperature of the spent catalyst is raised to higher temperatures is also within the scope of the present invention.

In order to maintain desired activity of the zeolite catalyst, it is desirable to regenerate the 25 catalyst under conditions of time, temperature and atmosphere sufficient to reduce the percent by weight of carbon remaining on the catalyst to about 0.05% or less, whether the catalyst bears a large heavy metals accumulation or not. The term coke, should be understood 30 to include any residual unvaporized feed or

hydrocarbonaceous material present on the catalyst after stripping thereof.

The substantial levels of conversion accomplished by the process of the present invention result in relatively large yields of coke, such as for example about 4% to about 17% by weight based on fresh feed, more commonly about 6% to about 14% and most frequently about 6% to about 12%.

At contemplated catalyst to oil ratios, the resultant coke laydown may be in excess of about 0.3%, more commonly in excess of about 0.5% and very frequently in excess of about 1% of coke by weight, based on the weight of moisture free virgin or regenerated catalyst. Such coke laydown may range as high as about 2%, or about 3%, or even higher, although coke in the range of 0.5 to about 1.5% is more commonly experienced.

According to a preferred embodiment of the present invention, the sub-process of regeneration, as a whole, may be carried out to the above-mentioned low levels of coke on regenerated catalyst with oxygen supplied to the one or more stages of regeneration in the stoichiometric amount required to burn all hydrogen in the coke to H_2O and to burn all carbon in the coke to CO and/or CO_2 and to burn all sulfur in the coke to SO_2 . If the coke includes other combustibles, the aforementioned stoichiometric amount can be adjusted to include the amount of oxygen required to burn them.

Multi-stage regeneration offers the technique of combining oxygen deficient regeneration with control

RI-6224A

of the $\text{CO}:\text{CO}_2$ molar ratio and still provide means by which coke on catalyst is reduced preferably to 0.05% or lower. Thus, about 65% to about 80% by weight of the coke on the catalyst is removed in a first stage of regeneration in which the molar ratio of $\text{CO}:\text{CO}_2$ is controlled.

In combination with the foregoing, the last weight percent of the coke originally present, up to the entire amount of coke remaining after the preceding stage can be removed in a subsequent stage of regeneration in which more oxygen is present.

A particularly preferred embodiment of the present invention is two-stage catalyst regeneration at a maximum temperature of about 816°C (1500°F) but preferably not above 760°C (1400°F). The second stage temperature is the same or lower than the first stage, with reduction of carbon on catalyst to about 0.05% or less or even about 0.025% or less by weight in the second zone. In fact, catalyst can readily be regenerated to carbon levels as low as 0.01% by this technique, even though the carbon on catalyst prior to regeneration is as much as about 1% or greater.

Still another particularly preferred technique for controlling or restricting the regeneration heat imparted to fresh feed via recycled catalyst involves the diversion of a portion of the heat borne by recycled catalyst to additional material, discussed herein. The catalyst discharged from the regenerator is stripped with appropriate stripping gases to remove oxygen containing gases. Such stripping may for instance be conducted at

relatively high temperatures, using steam nitrogen or inert gas(es) as the stripping gas. The use of nitrogen or other inert gases is beneficial from the standpoint of avoiding a tendency toward hydrothermal catalyst deactivation which may result from the use of steam.

FEEDSTOCK

The present invention is applicable to the catalytic conversion of light gas oil feeds or heavy residual oil feeds comprising vacuum bottoms and portions thereof which have been subjected to a previous partial hydrogenation operation to remove sulfur and nitrogen compounds, therefrom, and/or which has been partially decarbonized and demetallized by contact with a sorbent material under thermal visbreaking conditions in the presence of a diluent with or without the presence of hydrogen. The sorbent material employed in the visbreaking operation may be relatively inert or of such low catalytic activity that it is no longer suitable for use in a catalytic cracking operation. Thus, the essence of this invention is useful in the disclosed combination operation of U.S. 4,434,044 Busch et al,

The process conditions employed in the catalytic cracking operation of this invention will vary depending upon the composition and boiling range of the oil feed charged. Generally, the regenerated catalyst charged to the riser cracking operation will be at a temperature in the range of 649°C (1200°F) to 816°C (1500°F) and more usually about 704°C (1300°F) to 760°C

RI-6224A

B

(1400°F). The catalyst to oil ratio and hydrocarbon feed partial pressure will vary with the feed boiling range and volume of gaseous diluent used so that vaporous hydrocarbon conversion products comprising suspended cracking catalyst, 5 lift gas and feed atomizing diluent material zone at a temperature within the range of 482°C (900°F) to 598°C (1100°F) and more usually within the range of about 510°C (950°F) to about 566°C (1050°F).

The present processing concept of invention to 10 reduce coke, make and improve product selectivity is applicable to the processing disclosure of U.S. patent 4,434,044 as above identified with modification thereto as required in a metals removing oil feed decarbonizing visbreaking operation with solid sorbent fluid particles 15 followed by catalytic upgrading of the partially demetallized and decarbonized heavy oil feed by the technique of this invention. An important aspect of the combination operation of this referenced patent is related to the light gaseous product recovery steps of Figure 1, 20 wherein a fuel gas is recovered from a C₃-C₄ fraction. This fuel gas comprising hydrogen is particularly suitable when separated from the C₃-C₄ hydrocarbons for use in accordance with the processing concepts of the present invention. The processing concepts of the present 25 invention modify the cracking concepts of the references patent to the extent that dry gas without naphtha but comprising steam is used to form an upflowing suspension of the hot regenerated catalyst particle in a lower portion of the riser and, thereafter, contacted

30

X

with oil feed to be upgraded by crystalline zeolite catalytic cracking as herein provided.

In yet another aspect the apparatus arrangement of Figure V of U.S. Patent 4,434,044 comprising a riser catalytic cracking zone adjacent to a sequence of two stage catalyst regeneration providing for cooling of catalyst passed from said first stage to said second stage of catalyst regeneration is preferably modified to incorporate a riser reactor of larger diameter in an upper portion than in a lower portion thereof with the oil feed to be cracked being charged to a downstream section of the riser comprising the larger diameter portion, thereof. This riser design is a part of U.S. 4,435,279 Busch et al.

The simple but effective processing concepts comprising the essence of this invention are adaptable to any gas oil or lighter boiling residual oil catalytic cracking operation with the more recent crystalline zeolite catalysts developed for such purposes. Thus, the catalysts of U.S. 4,377,470; U.S. 4,407,714; U.S. 4,431,749; U.S. 4,432,890; and U.S. 4,440,868, may be used.

In a more particular aspect the present invention is a departure for reasons expressed below from the operation described and claimed in U.S. 4,431,515

B

Myers et al and U.S. 4,435,279 Busch et al.
These patents are related to the same field of catalytic
conversion of oil feeds as the present application.

5

The processing concepts and essence of this
invention depart from the above patents in several
different aspects including:

- 10 a) a refinery product gas known as dry gas
(commonly derived from the conventional gas
concentration unit, such as that shown in
Figure III of U.S. Patent 4,434,044 to Busch,
Walters and Zandona) comprising at least 10
15 vol.% of hydrogen but less than 10 vol.% of
 C_3 -plus materials is used as a suspension
forming lift gas for hot freshly regenerated
catalyst at a temperature of at least 704°C
(1300°F). The dry gas is supplemented with
20 steam and/or water as a heat sink in an amount
sufficient to reduce the regenerated catalyst
temperature to a desired low oil feed
conversion temperature. Preferred dry gas
contains about 15-40%, most preferably 20-35%
hydrogen and 2-8%, most preferably 0-6%
25 C_3 -plus.
- b) the dry gas-steam-catalyst suspension is formed
in the lower portion of a riser conversion zone
beneath the point of oil feed injection thereto
and retained for a residence time inhibiting
30 the deposition of coke on the catalyst from

RI-6224A

B

- exceeding about 0.20 wt% or 0.25 wt% before contact with charged oil feed boiling above about 343°C (650°F). Thus, the residence time of the formed suspension of dry gas-steam-regenerated catalyst in the riser prior to contact with charged oil is not more than a fraction of a second but sufficient to reduce metal oxides on the catalyst to a lower oxidation state or its metal state.
- 5
- 10 c) refinery product dry gas streams comprising less than 10 vol.% of C₃-plus material and from 10 to 40 vol.% hydrogen recoverable from an aromatic desulfurization unit and at economically attractive conditions which promotes the use thereof in the oil feed cracking operation of this invention. Hydrogen sulfide in this dry gas stream is an attractive ingredient to form sulfide compounds with the metal contaminants.
- 15
- 20 d) the processing of carbometallic oil feeds with catalyst comprising up to 20,000 ppm Ni+V metal contaminants accumulated on the catalyst may be accomplished with improved product selectivity using dry gas herein described when provided with one or more metal passivating agents or compounds for the nickel and vanadium accumulated on the catalyst.
- 25
- 30 e) the improved product selectivity achieved by the processing combination of this invention and contributing to substantially reduced

slurry oil and coke make contributes to reducing the temperature severity of the catalyst regeneration operation in the combination of regeneration stages from exceeding 760°C (1400°F) in either stage of regeneration. Thus, the hydrothermal catalyst deactivating conditions encountered with steam added to the dry gas to form a rising catalyst suspension is measurably reduced to acceptable limits.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph comparing the hydrogen yields obtained using a wet recycle gas and a dry recycle gas as catalyst lift gas prior to converting the oil feed to products boiling below 221°C (430°F).

Figure 2 is a graph comparing the C_5 221°C (430°F) gasoline yields obtained using a wet recycle gas and a dry recycle gas as a catalyst lift gas prior to converting an oil feed to products boiling below 221°C (430°F).

Figure 3 is a graph comparing the gasoline selectivity obtained using a wet recycle gas and a dry recycle gas as a catalyst lift gas prior to converting an oil feed to products boiling below 221°C (430°F).

Figure 4 is a graph comparing the coke yield obtained using a wet recycle gas and a dry recycle gas as catalyst lift gas when converting an oil feed to products boiling below 221°C (430°F).

Figure 5 is a graph comparing the C2-minus byproducts obtained when using a wet recycle gas and a dry recycle gas as a catalyst lift gas prior to converting an oil feed to products boiling below 221°C (430°F).

5 Figure 6 is a schematic diagram of the residual oil cracking unit - gas concentration section showing the recovery of suitable dry gas for use with the invention. Further description of this drawing may be found by referring to the corresponding figure III of U.S. 4,343,044 to Busch, Walters and Zandona.

10 Figure 7 is an alternate residual oil cracking unit reactor-regenerator more fully described by reference to corresponding figure V of U.S. 4,434,044.

15 Figure 8 is a diagrammatic arrangement of apparatus in elevation comprising two stage regeneration adjacent riser cracking.

DISCUSSION OF SPECIFIC EMBODIMENT

20 The processing concepts of the invention and resultant improvements obtained are identified particularly with the examples presented, the operating conditions employed and the results obtained as graphically depicted.

Table I identifies an analysis of a commercially obtained wet gas employed in the cracking process of the invention. It is to be noted that the

C₃-plus material up to and including C₅ hydrocarbon materials amounts to about 45%.

TABLE I

	<u>COMPOUND</u>	<u>MOLE %</u>
5	HYDROGEN	19.74
	METHANE	17.72
	NITROGEN	3.97
	CARBON MONOXIDE	0.72
	ETHYLENE	5.93
10	ETHANE	6.97
	OXYGEN + ARGON	0.03
	HYDROGEN SULFIDE	NOT DETECTED
	PROPYLENE	12.48
	PROPANE	4.16
15	CARBON DIOXIDE	1.13
	1,3-BUTADIENE	TRACE
	1-BUTENE + ISOBUTYLENE	5.07
	TRANS-2-BUTENE	2.59
	CIS-2-BUTENE	1.98
20	ISOBUTANE	3.81
	NORMAL BUTANE	1.08
	CARBONYL SULFIDE	TRACE
	ISOPENTANE	2.27
	NORMAL PENTANE	0.28
25	ELUTING AFTER N-PENTANE	10.05

Table II identifies an analysis of a commercially obtained dry gas employed in the cracking process of the invention. It is to be noted that the C₃-plus material up to and including N-Pentane is in an

amount of about 8.68%. Thus, it will be recognized that the commercial processing of refinery gaseous products to obtain an inexpensive dry gas product comprising less than 8 or 10% of C₃-plus material is economically difficult to achieve and, thus, of little or no interest to a petroleum refiner. It is desirable and essential on the other hand, to pass a suspension upwardly through a riser fluid catalyst cracking zone for contact with charged heavy oil feed. A light gaseous product of cracking is recovered in one aspect of this invention for recycle to the cracking operation and use, therein, as herein discussed.

TABLE II

	<u>COMPOUND</u>	<u>MOLE %</u>
15	HYDROGEN	20.01
	METHANE	33.10
	NITROGEN	9.94
	CARBON MONOXIDE	4.03
	ETHYLENE	12.70
20	ETHANE	11.40
	OXYGEN + ARGON	0.13
	PROPYLENE	4.24
	PROPANE	0.51
	CARBON DIOXIDE	0.01
25	1-BUTENE + ISOBUTYLENE	0.62
	TRANS-2-BUTENE	0.17
	CIS-2-BUTENE	0.11
	ISOBUTANE	0.69
	NORMAL BUTANE	0.12
30	ISOPENTANE	0.02
	ELUTING AFTER N-PENTANE	2.19

RI-6224A

In a sequence of experiments contributing to the recognition of the special concepts of the present invention, carbometallic containing residual oil feeds comprising Ramsbottoms carbon, sulfur, nickel and vanadium were brought in contact with a typical fluid cracking catalyst comprising a rare earth exchanged crystalline aluminosilicate (faujasite) containing cracking catalyst following regeneration, treatment thereof at an elevated temperature, herein defined with a dry gas hydrogen rich product comprising less than about 10% of C_3 -plus materials and a wet gas hydrogen rich product of catalytic cracking herein defined comprising substantial C_4 and C_5 hydrocarbons.

The considerable amount of data accumulated in the sequence of experiments was used to develop graphs I thru VII, herein below particularly discussed. The mixing of hot catalyst with dry or wet recycle gas as lift gas to form a catalyst suspension before contact with a residual oil feed is representative of a riser cracking operation herein after discussed.

FIGURE 1 - HYDROGEN PRODUCTION

Referring now to Figure 1, there is presented a plot of the data obtained with respect to hydrogen production obtained during conversion of a residual oil feed to 221°C (430°F) minus products after pretreatment of the cracking catalyst at a temperature of about 704°C (1300°F) with a hydrogen rich dry gas product or a

- hydrogen rich wet gas product. It will be observed from Figure I that the upper curve representing treatment of the catalyst with the wet gas product produced considerably more hydrogen during subsequent conversion of the residual oil feed with a catalyst suspension thereof than was obtained by using a dry gas as lift gas to form a suspension of high temperature catalyst of at least about 704°C (1300°F).

FIGURE 4 - COKE PRODUCTION

- Figure 4 is a further plot of the experimental data obtained showing the coke production obtained when converting a residual oil to 221°C (430°F) minus product in the presence of catalyst initially contacted with dry recycle gas or wet recycle gas employed as lift gas in, for example, a riser cracking zone. It will be observed from the plot of Figure 4 that the use of a hydrogen rich wet recycle gas comprising C₄ and C₅ hydrocarbons in substantial amounts produced considerable more coke in the catalyst than was obtained when using a hydrogen rich dry recycle gas. The high coke deposition contributes to obtaining high catalyst regeneration temperatures exceeding 760°C (1400°F).

FIGURE 2 - C₅ TO 221°C (430°F) GASOLINE YIELD

- Figure 2 on the other hand, identifies the C₅ to 221°C (430°F) gasoline yield provided by the experimental data when using a dry gas or a wet gas as a catalyst lift gas before contacting hot regenerated catalyst with the residual oil feed charged. It is significant to note from this figure that the use of dry

RI-6224A

A

gas as a lift gas provided higher yield of gasoline product than was obtained when using the wet gas as a lift gas. Thus, the gasoline product selectivity is considerably improved.

5

FIGURE 3 - GASOLINE SELECTIVITY

Figure 3 identifies from a plot of the experimental data, an improved gasoline selectivity curve obtained when using a dry gas to initially contact the hot regenerated catalyst over that obtained when using a hydrogen rich wet recycle gas, herein identified prior to converting the charged residual oil feed.

10

FIGURE 5 - REDUCED C2-MINUS BYPRODUCT

Figure 5, on the other hand, identifies the improved results obtained in the reduced C2-minus byproducts when employing dry and wet recycle gas product as herein defined. The figure shows that the yield of slurry oil is much less when using a dry recycle gas stream herein defined to initially contact the hot regenerated catalyst.

15

DATA ANALYSIS OF FIGURES 1 - 5

Some conclusions drawn from an evaluation of the self-explaining briefly discussed data plots identifies beyond any reasonable doubt that a wet recycle gas comprising substantial amounts of C_3 plus hydrocarbons found in a wet gas contributes coke to the cracking catalyst, thereby reducing the catalyst cracking activity and selectivity as shown by the yield difference obtained in C_5 plus gasoline and light cycle oil yield. Using a dry gas, on the other hand, comprising very little C_3 plus materials comprising C_4 and C_5 product material provided improved yields. It is further noted that when using a dry gas composition defined herein permits one to use from about 12 to 15 weight percent more lift gas relative to feed in a given riser cracking

RI-6224A

operation. When the lift gas comprises a significant quantity of C_3 plus material comprising C_5 hydrocarbons which are cracked to deposit coke on the hot freshly regenerated catalyst prior to contact with the residual oil feed, thereby reducing the catalyst cracking activity and selectivity as shown by the above discussed figures, this contributes to a resultant loss in C_5 plus gasoline product material evaluated to amount to at least 3 to 5 vol.% of desired gasoline forming product material. The resultant precoked catalyst is found to provide increased slurry oil and coke make as shown by the graphs presented as self explanatory.

It is thus clear from the experimental evidence obtained and plotted to form the graphs herein discussed, that it is essential to more efficient riser cracking of oil feeds, to use a lift gas initially in contact with hot freshly regenerated catalyst which contributes little, if any, coke deposition on the hot catalyst particles prior to contact with the oil feed to be converted. This operating concept is accomplished as determined by the experimental evidence herein provided by using an economically obtainable commercial dry gas product of a refinery operation such as the cracking operation comprising hydrogen and preferably less than about 10% of C_3 plus hydrocarbons. Another lift dry gas suitable for the purpose is one consisting of hydrogen, methane and ethane. However, such a recycle lift gas product stream of a cracking or refinery operation is difficult to obtain economically from a commercial operation. A hydrogen-containing gas stream obtained from desulfurizing an aromatic oil product of coal

processing may be used provided the C_3 plus hydrocarbons therein are less than 10 vol. percent.

It is concluded further from the available evidence directed to the processing concepts of this invention that the regenerated catalyst should be reduced to a residual coke level of at least 0.10 wt% and preferably to at least 0.05 wt%. The formed catalyst suspension with dry gas and comprising hydrogen prior to contact with the oil feed to be converted should be restricted to a coke level not to exceed about 0.20 wt% and preferably should not be above about 0.15 wt% to reap the significant benefits of the herein identified operating concepts.

The regenerated catalyst-dry gas suspension forming concept of the present invention is applicable to a fluidized catalyst riser contact system such as provided by U.S. Patents 4,435,279 and 4,434,044. Modification of these patent disclosures to encompass the operating concepts of this invention will contribute to improving the operations thereof in a most favorable direction.

APPARATUS RISER:

20

The specific apparatus arrangement of Figure 7 provided herewith corresponds substantially to Figure I of U.S. Patents 4,435,279 and Figure V of U.S. Patent 4,434,044. In alternate apparatus shown in Figure 8 there is provided a riser reactor 1 with an expanding transition section in an upper portion thereof which terminates in a larger diameter

25

portion 2 of the riser there above. Conversion of the charged oil feed such as a residual oil feed by one of 5, 7 or 9 feed inlets is particularly effective. The expanded or larger diameter portion of the riser 2 is provided with a plurality of feed inlet nozzles means 6 adjacent the upper edge of the transition section which are used in a preferred embodiment to charge the oil feed. The vertically spaced apart feed inlet means 5, 7 and 9 provides the operator considerably more latitude in feed contact time with the dry gas-catalyst suspension within the riser reactor before separation of a resultant formed suspension of hydrocarbon product vapors, catalyst and lift gas available as herein discussed. Thus, the riser 1-2 configuration of Figure VIII permits achieving relatively high temperature zeolite catalytic upgrading of an oil feed charged to a bottom, intermediate or upper portion of the riser conversion zone but downstream of the formed dry gas-regenerated catalyst suspension to restrict the oil feed contact time with catalyst within the range of a fraction of a second up to 1, 2 or even 3 seconds contact time.

In this riser arrangement, the hot regenerated catalyst at a temperature within the range of 649°C (1200°F) to 816°C (1500°F) is initially mixed with a dry lift gas or fluidizing gas as herein provided with the addition of steam and/or water as heat sink material to form an upflowing suspension in the restricted diameter portion thereof at a temperature suitable for effecting catalytic cracking of a downstream charged residual oil feed as by 7 or 9. Thus, feed inlet means a 5, 7 and 9 with diluent inlets 6, 8 and 10 permit a substantial variation in feed atomization and partial pressure and

contact time as above identified between oil feed and the dry gas-steam suspended catalyst particles. Furthermore, a bottom portion of the riser reactor permits adjustment of the regenerated catalyst temperature by the addition of steam and/or water as a heat sink along with the dry lift gas of a composition particularly identified herein.

Generally speaking the contact time between a residual oil feed and catalyst in the riser depending on feed composition and source will be restricted to within the range of 0.5 to about 2 or 3 seconds when contacting an oil feed with catalyst at a temperature in the range of 704°C (1300°F) to 760°C (1400°F) to provide a riser outlet temperature within the range of 510°C (950°F) to 593°C (1100°F) and more usually not above 566°C (1050°F). The riser reactor may be substantially any desired vertical length which will be compatible with the adjacent catalyst regeneration apparatus whether of single or multiple stages of regeneration as shown, catalyst stripping and catalyst transfer conduit means essential to the combination.

STRIPPING:

The upper portion of riser 2 passes upwardly through a stripping zone 6 to form an annular stripping zone therewith into an upper portion of a larger diameter catalyst disengaging zone in open communication with the annular stripping zone 16. Stripping gas such as steam or other suitable gas is charged to a bottom portion of the stripping zone by conduit 17 for flow upwardly therethrough and counter-current to downflowing catalyst particles.

REGENERATION:

The stripped catalyst is then passed by conduit 19 to catalyst regeneration shown as a sequence of catalyst beds 20 and 36 being regenerated in separate zones to remove carbonaceous deposits of conversion by combustion without exceeding an elevated temperature below about 816°C (1500°F) and preferably restricted to within the range of about 649°C (1200°F) to 816°C (1500°F) and more usually within the range of 704°C (1300°F) to 760°C (1400°F).

CATALYST SEPARATION:

An important aspect of the riser system of this invention is particularly concerned with the method and means for separating the upwardly flowing suspension at the riser upper open end. That is, the suspension of hydrocarbon vapors, catalyst, lift gas and steam is discharged from the upper open end of the riser at a velocity which will impart a greater momentum to the particles of catalyst than to that imparted to the vaporous constituents whereby an upwardly flowing trajectory is established which separates catalyst particles from vaporous material. The vaporous material mixture, often referred to as gasiform material in the prior art, passes into an annular cup 11 withdrawal passageway open in the top thereof and thence through radiating conduit means in open communication with cyclone separation means 12 on the outer end of each of said radiating conduits. Vapors separated from entrained catalyst fines in cyclones 12 are recovered by conduits communicating with plenum chamber 13 and product

withdrawal conduit 14 for passage to product fractionation and separation in means not shown. Catalyst fines separated in cyclones 12 are removed by diplegs for passage to catalyst stripping and regeneration discussed below.

CATALYST:

The hydrocarbon conversion operation contemplated to be accomplished in the riser zone herein discussed relies upon the use of fluidizable particles of catalyst of a particle size in excess of 10×10^{-6} meters (10 microns) and usually providing an average particle size within the range of 60 to 100×10^{-6} meters (60 to 100 microns) and more usually below about 85×10^{-6} meters (85 microns). The catalyst is preferably one comprising a crystalline aluminosilicate or crystalline zeolite which has been rare earth and/or ammonia exchanged to provide a catalytically active material which is dispersed in a matrix material which may or may not have catalytic activity. A catalyst particularly suitable for use in the process of this invention is a rare earth exchanged faujasite crystalline zeolite comprising a catalyst pore volume and matrix pore size openings which will collect and/or accumulate substantial quantities of metal contaminants and yet retain substantial catalyst cracking activity and selectivity as herein provided.

FEEDS:

The oil feed such as a residual portion of crude oil charged by feed inlet 5 or 7 may be mixed with

steam and/or water such as product sour water charged by conduits 6 or 8. On the other hand, when charging the oil feed by feed inlet 9, the steam-water mixture may be added by conduit 10. The bottom portion of riser 2 is provided with dry lift gas inlet conduit 4 for charging the lift gas to form a upflowing suspension with hot regenerated catalyst particles charged to a bottom portion of the riser by conduit 3. The dry lift gas may be charged to the riser alone or in combination with steam and/or water introduced by conduit 43.

The lower portion of the riser of restricted diameter may be used to serve several different functions beyond the formation of an upflowing suspension of a desired catalyst particle concentration within the range of 16 to 44 kilograms per cubic meter. That is, the use of a hydrogen containing dry gas herein identified as lift gas may be used as a contaminant metals passivation material to which a passivating metal compound is added to passivate Ni and V. Antimony may be added to passivate accumulated nickel deposits. Vanadium oxide may be passivated by the combination of hydrogen reduction to a lower oxide state providing a high melting point oxide thereof alone or in conjunction with the addition of titanium, alumina and rare earth metals rich in lanthanum. Thus, whatever use is made of the lower portion of the riser reactor prior to oil feed atomized injection, it is essential to the concepts of this invention that the use of a hydrogen containing product recycle dry gas be of a composition which severely limits the C_3 plus components of the dry gas to a level inhibiting any significant coking of the catalyst therewith and prior to contact with the heavy oil feed to

be cracked. As particularly discussed, herein, restricting the hydrogen containing dry gas to a C_3 plus content less than 10%, more preferably less than 8% and most preferably less than 6%, improves the gasoline yield, reduces the yield of hydrogen, increases the yield of light cycle oil and reduces the yield of slurry oil and coke. These findings obtained by experimental evidence where unexpected and not predictable. A further significant economic aspect of the operating concept is the use of readily available refinery product gases or other source gases comprising from 10 to 40 vol. percent of hydrogen in the dry gas.

In a particular operating embodiment, a dry gas product of the cracking operation is employed comprising at least 15 vol. percent hydrogen, less than 10 vol.% of C_3 plus hydrocarbons in admixture with water in an amount sufficient to partially cool the regenerated catalyst to a desired low oil feed conversion level before contact with atomized preheated residual oil charged to the rising dry gas-steam-catalyst suspension. The fluid catalytic cracking of the charged hydrocarbons is effected at a riser pressure above atmospheric pressure and the riser cracking operation of this invention may be effected at a pressure of about 172×10^3 to $1,137 \times 10^3$ Pascals (about 10 to 150 psig) pressure. However, the atomized oil feed hydrocarbon partial pressure will be substantially reduced by the lift gas-steam mixture and the oil feed atomizing diluent material. Thus, the oil feed partial pressure may be in the range of 27.6 to 172×10^3 Pascals and the catalyst to oil ratio may be within the range of about 5 to 15, more preferably 6 to 12, and

providing for intimate contact between catalyst particles and the atomized oil feed.

5 The combustion apparatus of Figure VIII provides a unique catalyst particle regeneration arrangement permitting close temperature control to minimize particularly hydrothermal deactivation of catalyst particles during the removal of coke deposits by combustion and contributed particularly by gas oil catalytic conversion and/or higher boiling components of
10 residual oil including vacuum resid.

Referring now particularly to the catalyst regeneration apparatus and its method of utilization there is provided a unique arrangement in that the upper chamber portion thereof is of a larger diameter than a
15 bottom chamber portion and separated from one another by a regeneration gas distributor chamber 24 centrally located and supported by an annular baffle member 40 provided with gas flow through passage ways 41. A plurality of radiating arm means 25 from chamber 24 are provided for introducing regeneration gas to a lower
20 bottom portion of catalyst bed 20 being regenerated. Regeneration combustion supporting gas such as air or an oxygen modified gas in conduit 22 admixed with steam in conduit 23 provides a desired concentration of oxygen and
25 amounting to more or less than that required to achieve a partial removal of carbonaceous deposits from the charged catalyst particles whereby combustion temperatures encountered can be restricted to within a desired range are charged by plenum 24 and radiating arms 25. In this
30 first stage of catalyst regeneration comprising combustion of hydrocarbonaceous deposits effected in the

presence of oxygen, carbon dioxide and steam as desired, the regeneration temperature is preferably kept to a low value in the range of 593°C (1100°F) to 871°C (1600°F), preferably 649°C (1200°F) to 815°C (1500°F) and more usually in the range of about 690°C (1275°F) to 760°C (1400°F).

A partial removal of carbonaceous material is removed in catalyst bed 20 under conditions producing CO rich containing product flue gases and comprising carbon dioxide, sulfur, nitrogen and water vapor. The, thus, generated flue gases pass through one or more combination of cyclones represented by cyclones 26 to remove entrained catalyst fines recovered by diplegs provided. The flue gases then pass from cyclones 26 to a plenum chamber 27 for recovery therefrom by conduit 28. Such CO rich containing flue gases are normally passed to a CO boiler not shown to generate process steam.

The partially regenerated catalyst comprising bed 20 is removed from a bottom portion thereof for downflow through an external catalyst cooling zone 29 in indirect heat exchange with bayonet type heat exchange tubes 30 provided and substantially vertically extending therein. High pressure steam of the order of about 3.1×10^6 Pascals (450 pounds) steam is generated and recovered as by conduit 34 when charging boiler feed water by conduit 31 to a distributor chamber in the bottom of cooler 29 communicating with said heat exchange tubes 30. The catalyst partially cooled in chamber 29 by an amount in the range of 28°C to 111°C (50°F to 200°F) and more usually in the range of 55 to 83°C (100 to 150°F) is withdrawn and passed by conduit 35 to a bed of catalyst

36 retained in the second stage of catalyst regeneration in chamber 37. A stand pipe 42 communicating between bed 20 and 36 is provided for direct passage of catalyst without cooling from the upper bed to the lower bed when required. However, the main or primary flow of catalyst between beds is through cooler 29 to maintain desired catalyst temperature restraints in the sequential regeneration system. A temperature restraint in the second stage comprising bed 36 is restricted within the range of 649°C (1200°F) to 816°C (1500°F) and more usually within the range of 704°C (1300°F) to 760°C (1400°F). The temperature of the regenerated catalyst in dense fluid bed 36 may be equal to, above or below the temperature maintained in dense fluid catalyst bed 20 in the first stage of catalyst regeneration. In one embodiment, the amount of air or oxygen modified gas charged to catalyst bed 36 by conduit 38 and passing through grid 39 may be equal to or more than that required to complete combustion of residue carbon on the partially regenerated catalyst and provide a CO₂ rich flue gas product which may or may not comprise some unconsumed oxygen. It is preferred that the flue gas passed from the upper dense phase of catalyst bed 36 be free of combustion supporting amounts of CO to prevent after burning from occurring therein. The CO₂ rich flue gas product of the second stage of catalyst regeneration at an elevated temperature passes through openings 41 in baffle 40 into a bottom portion of bed 20 for admixture with the regeneration gas charged by distributor arms 25 thereby contributing heat to the first stage of catalyst regeneration. All of the flue gas combustion products of the second stage of catalyst regeneration to reduce the coke residue to about 0.05 wt% or as low as about 0.01

wt% coke on regenerated catalyst particles passes through catalyst bed 20 of the first stage of regeneration. Regenerated catalyst obtained as above provided is withdrawn from an upper catalyst bed 36 for passage by conduit 3 to a bottom portion of riser 1 for use as above discussed.

In an apparatus arrangement disclosed and discussed with respect to Figure VIII it is contemplated employing a riser reaction zone of a vertical length of about 49 meters (about 160 feet) through which a catalyst suspension is passed at a velocity in the range of 18 to 31 meters/sec (60 to 100 ft/sec.). In a specific embodiment employing a velocity of about 24.5 meters/sec (80 ft/sec) the suspension traverses the riser in about 2 seconds. In such an operation the dry gas-steam-catalyst suspension initially formed consumes a residence time of a fraction of a second up to 0.5 second before contact with the atomized oil feed and providing a hydrocarbon residence contact time with catalyst particles up to about 1 or 1.5 seconds. The short residence times identified are not detrimental to the process and may be used with considerable advantage to maintain desired product selectivity by reducing any tendency of over-cracking to occur.

It will be understood by those skilled in the art that the invention is not to be limited by the above examples and discussions and that the examples are susceptible to a wide number of modifications and variations without departure from the invention.

RI-6224A

B

WHAT IS CLAIMED IS:

1. In a process for effecting the catalyst cracking of an oil feed fraction of crude oil with a crystalline zeolite containing cracking catalyst in a riser cracking zone, the improved method of operation which comprises,
 - a) employing a dry gas comprising at least about 10 mol% hydrogen and less than 10 vol.% of C_3+ material as a lift gas to form a rising suspension of catalyst particles at an elevated hydrocarbon conversion temperature,
 - b) maintaining contact between said lift gas and the suspended catalyst particles for a limited contact time of from 0.01 to 2 seconds, maintaining deposition of coke on the catalyst by said dry gas from exceeding 0.20 weight% prior to contact with said oil feed to be converted and
 - c) contacting said catalyst suspended in dry gas with said oil feed under temperature conversion conditions, whereby there is provided improved product selectivity to gasoline and light cycle oil.
2. In a process for cracking heavy oil fractions of a crude oil with a crystalline zeolite catalyst comprising accumulated metal contaminants of Ni and V, the improved method which comprises,

RI-6224A

- 5 a) initially contacting metal contaminated regenerated catalyst at a temperature of at least about 704°C with a lift gas comprising steam and water to form a suspension of desired reduced temperature, said lift gas comprising refinery product recycle gas comprising hydrogen and less than 10 vol.% of C₃ plus hydrocarbons,
- 10 b) maintaining said lift gas-steam mixture in contact with said metal contaminated catalyst for a time sufficient to reduce said metal contaminants prior to contact with oil feed,
- 15 c) providing one or more metal compounds in said lift gas-catalyst suspension which will passivate said accumulated Ni and V metal contaminants on said catalyst,
- 20 d) cracking said heavy oil fraction with said dry gas-steam-catalyst suspension,
- e) recovering a product of catalytic cracking of improved selectivity to gasoline and light cycle oil yield, and
- f) recovering said gasoline and cycle oil from said catalyst.

3. The process of claim 2 wherein the heavy oil
25 fraction comprises vacuum gas oil.

4. The process of claim 2 wherein the heavy oil fraction is a residual portion of crude oil boiling above 343°C (650°F).
5. The process of claim 2 wherein said refinery product recycle dry gas is a gaseous product of catalytic cracking.
6. The process of claim 2 wherein the refinery product recycle gas is a gaseous product of desulfurization comprising hydrogen sulfide.
- 10 7. The process of claim 2 wherein the lift gas-steam mixture is in contact with said high temperature regenerated catalyst for a fraction of a second in an initial portion of a riser cracking zone before contact with the heavy oil feed charged in a
- 15 highly atomized condition.
8. The process of claim 7 wherein the lift gas-steam mixture is in contact with said high temperature regenerated catalyst for a fraction of a second in the range of 0.1 to 0.5 second.
- 20 9. The process of claim 2 wherein the catalyst comprises an accumulation of metal contaminants in the range of 1000 to 20,000 ppm Ni + V.
10. The process of claim 2 wherein the lift gas comprises greater than 10 vol. percent of hydrogen and
- 25 the regenerated catalyst at a temperature of at least 704°C (1300°F) comprises not more than about .05 wt% residual coke.

11. The process of claim 10 wherein the formed suspension of lift gas-steam and regenerated catalyst comprises less than 0.2 wt% coke on catalyst when contacted with oil feed in a downstream portion of the riser reaction zone.

12. The process of claim 11 wherein the suspension of lift gas-steam and regenerated catalyst comprises a deposition of coke restricted to within the range of 0.1 to about 0.15 wt% at the time of contact with charged oil feed.

13. The process of claim 12 wherein the catalyst temperature is reduced by the lift gas-steam mixture sufficient to provide a riser outlet temperature within the range of 510 to 566°C (950 to 1050°F) following conversion of the charged oil feed.

14. The process of claim 2 wherein the accumulated metal contaminants are passivated with one or more of antimony, titanium, chromium, zirconium and lanthanum rich rare earths.

15. In a process for catalytically converting oil feeds providing a Ramsbottom carbon value in the range of 0 to 6 with crystalline zeolite catalysts comprising accumulated metals of nickel and vanadium to produce liquid fuel products comprising gasoline and light cycle oil, the improvement which comprises,

a) regenerating said catalyst to a residual coke level less than about 0.05 wt.% thereby heating

said catalyst to a temperature of at least about 704°C (1300°F),

- b) partially cooling said regenerated catalyst by contact with a hydrogen rich lift gas comprising less than 10 vol.% of C₃ plus hydrocarbon in admixture with steam and water whereby residual coke on the regenerated catalyst is maintained below 0.2 wt.% and metal contaminants are reduced and passivated with metal additives, and
- c) contacting the partially cooled regenerated catalyst in a riser cracking zone with at least a gas oil containing feed under temperature conditions and contact time providing improved selectivity in gasoline and light cycle oil yields.

16. The process of claim 15 wherein the regeneration of the catalyst is accomplished in two sequential stages of regeneration maintained at a temperature within the range of 704°C to 760°C (1300 to 1400°F) and cooling of the regenerated catalyst with said lift gas-steam-water mixture is sufficient to limit the hydrocarbon product of catalytic conversion at the riser outlet within the range of 510 to 566°C (950 to 1050°F).

17. In a process for the catalytic conversion of a hydrocarbon oil feed with a crystalline zeolite conversion catalyst, the improvement which comprises,

- a) forming a suspension of hot freshly regenerated catalyst with a hydrogen rich dry gas comprising less than 10 vol.% of C_3 plus gaseous hydrocarbons for a time whereby coke deposition on the catalyst is limited not to exceed about 0.2 wt.%, and
- 5
- b) thereafter contacting said suspension of dry gas and catalyst with a $343^{\circ}C$ ($650^{\circ}F$) plus oil feed providing a Ramsbottom carbon value within the range of 0 to 8 at said oil feed hydrocarbon conversion conditions providing a vaporous product at a temperature within the range of 482 to $593^{\circ}C$ (900 to $1100^{\circ}F$).
- 10
18. In a process for the catalytic conversion of an oil feed providing a Ramsbottom carbon level in the range of 0 to 8 with a crystalline zeolite cracking catalyst comprising metal contaminants of at least 1000 ppm nickel plus vanadium, the improvement which comprises,
- 15
- a) recovering regenerated catalyst from a catalyst regeneration zone at a temperature within the range of 649 to $816^{\circ}C$ (1200 to $1500^{\circ}F$),
- 20
- b) mixing said recovered regenerated catalyst with steam and a hydrogen rich dry gas comprising primarily C_3 and lower boiling hydrocarbon in an amount to form an upflowing mixed suspension thereof of desired hydrocarbon conversion temperature, and
- 25

- c) contacting said oil feed to be converted to lower boiling products with said suspension for a time limited to providing a vaporous conversion product at a temperature in the range of 482 to 593°C (900 to 1100°F).

19. In a process for cracking oil fractions of crude oil boiling above 343°C (650°F) with a crystalline zeolite cracking catalyst, the improved method of operation which comprises,

- a) forming a high temperature suspension of hydrogen rich dry gas with regenerated catalyst at a temperature above 649°C (1200°F) for a fraction of a second limiting coke on the catalyst from exceeding 0.2 wt.%,
- b) contacting said suspension thus formed with said oil feed in an amount providing a vaporous hydrocarbon conversion product temperature within the range of 482 to 566°C (900 to 1050°F) and
- c) recovering a product of said hydrocarbon conversion of improved selectivity in gasoline and light cycle oil yield.

20. In a process for cracking carbometallic residual oil feed stocks containing hydrocarbon components which do not boil below 552°C (1025°F), greater than 10 ppm nickel plus vanadium and a Ramsbottom carbon value of at least 4, the improvement which comprises,

RI-6224A

- 5 a) contacting said residual oil feedstock preheated to a temperature in the range of 177 to 371°C (350 to 700°F) in a riser cracking zone with a regenerated cracking catalyst at an initial temperature in the range of 649 to 816°C (1200 to 1500°F) for a contact time of 1 to 4 seconds to obtain a vaporous hydrocarbon product of residual oil conversion, .
- 10 b) said cracking catalyst characterized by a metals content greater than 1000 ppm nickel plus vanadium, a carbon content prior to contact with said residual oil feed less than 0.2 wt.% and a catalytic crystalline zeolite content within the range of 5 to 40 wt.%,
- 15 c) separating the vaporous hydrocarbon product of conversion from catalyst by the technique of ballistic separation,
- d) stripping the separate catalyst to remove entrained liquid and vaporous materials,
- 20 e) passing the stripped catalyst to the first stage of a two stage catalyst regeneration operation to remove by combustion from 20 to 90 wt% of deposited carbonaceous material thereby raising the catalyst temperature within the range of 649 to 816°C (1200 to 1500°F),
- 25 f) passing partially regenerated catalyst to a separate second catalyst regeneration zone to remove residual coke thereon to a level of at

least 0.05 wt% or less under conditions restricting the catalyst temperature within the range of 649 to 816°C (1200 to 1500°F),

- 5 g) passing the catalyst thus regenerated to a bottom portion of a riser cracking zone for contact with a hydrogen rich dry gas to form an upflowing suspension thereof and passing said formed suspension upwardly through said riser cracking zone for a residence time up to about 10 1 second before contact with said residual oil feed, and
- h) catalytically converting said residual oil feed in said cracking zone with said catalyst characterized in (b) above to form vaporous 15 conversion products at a temperature within the range of 482 to 566°C (900 to 1050°F).

21. The process of claim 20 wherein said vaporous conversion products are separated to recover liquid products from gaseous products and said gaseous products 20 are separated to recover a hydrogen rich dry gas product comprising less than about 10 vol. percent of C₃ plus hydrocarbons and recycling said separated hydrogen rich dry gas product to said riser cracking zone to form said suspension with regenerated catalyst particles.

25 22. The process of claim 20 wherein steam with or without water is added with said hydrogen rich dry gas to the riser cracking zone to adjust the temperature of the regenerated catalyst charged thereto.

23. The process of claim 20 wherein said residual oil feed comprises from 5 to 300 ppm Ni + V and said catalyst comprises between 1000 and 20,000 ppm of Ni + V.

24. In a process for converting a carbometallic
5 containing oil feed containing a 343°C (650°F) plus
fraction of crude oil characterized by a Ramsbottom
carbon level in the range of 0 to 8 and comprising
contaminant metals of nickel and vanadium, said oil feed
10 contacted with a hot cracking catalyst comprising at
least 1000 ppm of nickel plus vanadium in a riser
cracking zone for a hydrocarbon residence time less than
3 seconds whereby vaporous hydrocarbon conversion
products of catalytic cracking are formed at a
15 temperature in the range of 482 to 593°C (900 to 1100°F)
and carbonaceous deposits of cracking are deposited on
said cracking catalyst, the cracking catalyst is separated
from vaporous hydrocarbon products upon discharge from
said riser cracking zone by ballistic separation for
20 separate recovery thereof, the separated catalyst is
stripped of volatile hydrocarbons prior to effecting
restricted temperature regeneration thereof not to exceed
about 760°C (1400°F) by combustion of carbonaceous
deposits with an oxygen containing gas in a sequence of
25 catalyst regeneration zones and the hot regenerated
catalyst is returned to said riser conversion zone for
conversion contact of charged oil feed, the improvement
which comprises,

a) forming a suspension of said hot regenerated
30 catalyst with steam and with dry gas comprising
less than 40 vol.% of hydrogen and less than 10
vol.% of C₃ plus hydrocarbons,

b) said formed suspension passed upwardly through an initial portion of the riser hydrocarbon conversion zone in the absence of charged oil feed for a residence time effecting reduction of metal oxides of regeneration and passivation thereof by additive materials suitable for the purpose, and

c) passing the oil feed to be converted in atomized contact with said formed suspension in a downstream portion of said riser cracking zone.

25. The process of claim 24 wherein said dry gas comprises at least 10 vol.% of hydrogen.

26. The process of claim 24 wherein said dry gas comprises a dry gas product of hydrogenation treatment of heavy oil aromatics comprising sulfur compounds.

27. The process of claim 24 wherein said catalyst is regenerated to contain not more than 0.05 wt% residual coke and comprises not more than 0.2 wt% coke in the formed suspension at the time of contact with said oil feed.

28. The process of claim 27 wherein coke on the regenerated catalyst is less than 0.05 wt%.

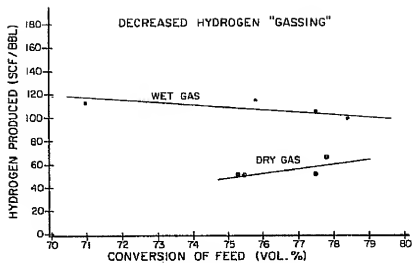
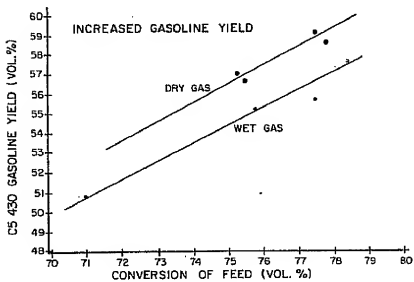
29. The process of claim 24 wherein the charged oil feed is a vacuum gas oil.

30. The process of claim 24 wherein the charged oil feed is a residual fraction of crude oil comprising components which do not boil below 552°C (1025°F).

5 31. The process of claim 24 wherein an accumulation of nickel and vanadium contaminants on the catalyst is within the range of 1000 to 20,000 ppm and the metals contaminated catalyst is partially replaced with a higher activity catalyst of lower metals content.

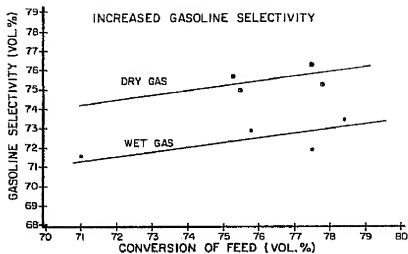
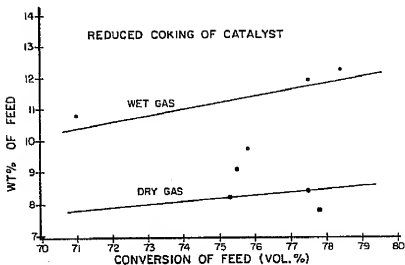
1265464

6-1

FIG. 1FIG. 2*Gosling & Henderson*

1265464

6-2

FIG. 3FIG. 4*Gowling & Henderson*

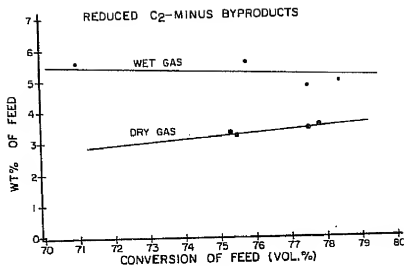


FIG. 5

Gowling & Henderson

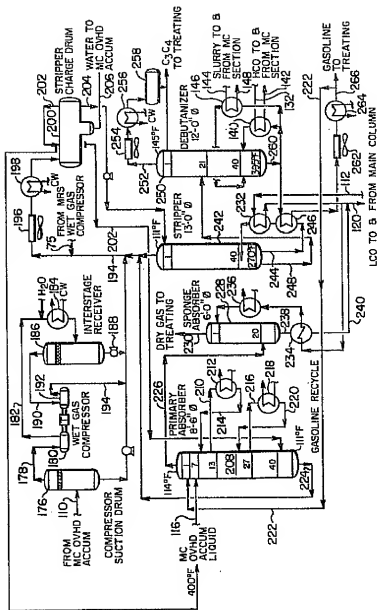
1265464

6-4

FIG. 6

RESIDUAL OIL CRACKING

UNIT - GAS CONCENTRATION SECTION

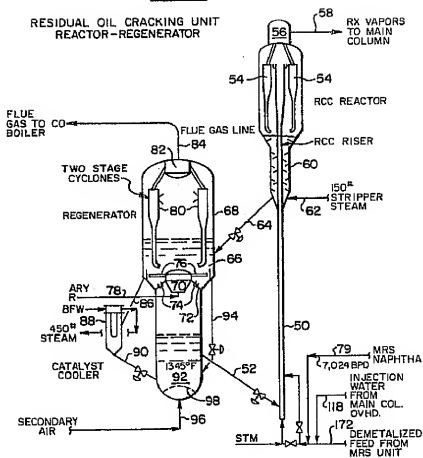


Gowling & Henderson

1265464

5-7

FIG. 7



Gowling v. Henderson

